

Containment Barrier Metals for High-Level Waste Packages in a Tuff Repository

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October 12, 1983

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Abstract

The Nevada Nuclear Waste Storage Investigations (NNWSI) Waste Package project is part of the U.S. Department of Energy's Civilian Radioactive Waste Management (CRWM) Program. The NNWSI project is working towards the development of multibarriered packages for the disposal of spent fuel and high-level waste in tuff in the unsaturated zone at Yucca Mountain at the Nevada Test Site (NTS). The final engineered barrier system design may be composed of a waste form, canister, overpack, borehole liner, packing, and the near field host rock, or some combination thereof. Lawrence Livermore National Laboratory's (LLNL) role is to design, model, and test the waste package subsystem for the tuff repository.

At the present stage of development of the nuclear waste management program at LLNL, the detailed requirements for the waste package design are not yet firmly established. In spite of these uncertainties as to the detailed package requirements, we have begun the conceptual design stage. By conceptual design, we mean design based on our best assessment of present and future regulatory requirements. We anticipate that changes will occur as the detailed requirements for waste package design are finalized.

Introduction

We have selected a few candidate metals for conceptual design of overpacks and canisters. Samples of these metals will be subjected to corrosion tests under repository conditions. Important materials-property data were developed to reflect engineering design requirements for potential candidate materials. The metals that were initially considered fall into the following categories: austenitic stainless steels, ferritic stainless steels, duplex stainless steels, high-nickel alloys, titanium alloys, zirconium alloys, copper-nickel alloys, low-carbon steels, and cast irons. These metals are all commercially available.

Our procedure involved determining and evaluating the properties considered to be important. These fall into four general categories:

- General and local corrosion resistance (including welded and heat-affected zones).
- Material and fabrication costs.
- Desired mechanical properties.
- Weldability.

This analysis has resulted in the selection of four metals for canister and overpack materials, and one metal for horizontal borehole liners:

1. AISI 304L stainless steel.
2. AISI 321 stainless steel.
3. AISI 316L stainless steel.
4. Incoloy 825 nickel-base alloy.
5. AISI 1020 carbon steel (for horizontal borehole liners only).

Reference designs for defense high-level waste (DHLW), commercial high-level waste (CHLW), and spent fuel (SF) canisters have been selected from several LLNL conceptual designs. The reference designs may not necessarily be our preliminary or final design configurations, but we are focusing our attention on them during the conceptual design period. For the DHLW package, the AISI 304L stainless steel pour-canister, which will be used to cast the glass at the waste reprocessing plant, has been selected for vertical emplacement into boreholes beneath

the drift floors, and a similar but smaller pour canister has been selected for CHLW (see Figs. 1 and 2). For both boiling-water reactor (BWR) and pressurized-water reactor (PWR) spent fuel, the reference design is an AISI 304L stainless steel canister that will house consolidated fuel rods for vertical emplacement (see Fig. 3).

The reference canister and overpack metal is AISI 304L stainless steel, but alternative metals

will also be considered for the following two reasons: (1) to provide a replacement material until the reference material is confirmed by testing under site specific conditions, and (2) to provide comparative data to support the choice of AISI 304L stainless steel as the reference material during the regulatory review.

Design Requirements and Constraints

We are designing waste packages to meet the Final Rule, NRC 10CFR, Part 60, and derivative requirements.^{1,2} To comply with these, we have developed the list of design requirements given in Table 1. These requirements pertain to the disposal of defense high-level waste, commercial high-level waste, and spent fuel.

Designs

The waste package designs considered in the evaluation and selection of metals for canisters, overpacks, and liners are as follows^{2,3}:

- 1.0 Reference designs emplaced in vertical boreholes with no liner and no packing.
 - 1.1 DHLW: emplacement of 61-cm-diam 304L pour canister, 1-cm thick.
 - 1.2 CHLW: emplacement of 32-cm-diam 304L pour canister, 1-cm thick.
 - 1.3 Spent fuel: emplacement of consolidated spent fuel rods in a 304L canister, 1-cm thick.

These dimensions are assumed by LLNL at this time for conceptual design purposes only.

- 2.0 Alternative designs for vertical boreholes.
 - 2.1 Alternative metals to 304L for canisters and overpacks.
 - 2.2 Overpacks for DHLW and CHLW for those canisters which do not meet acceptance criteria when received at the NNWSI repository.

- 2.3 Use of packing for spent fuel canisters, if the engineered system does not meet the release rate requirement.

- 3.0 Horizontal emplacement of waste packages within steel borehole liners.

Meeting the design requirements listed in Table 1 involves determining and evaluating the engineering properties considered to be important. Engineering properties are those physical characteristics (corrosion resistance, fracture toughness, weldability, cost, etc.) which significantly affect the performance of the canister and overpack functions in meeting the design requirements cost-effectively. Thus, the four general categories were established:

- General and local corrosion resistance.
- Material and fabrication costs.
- Mechanical properties.
- Weldability.

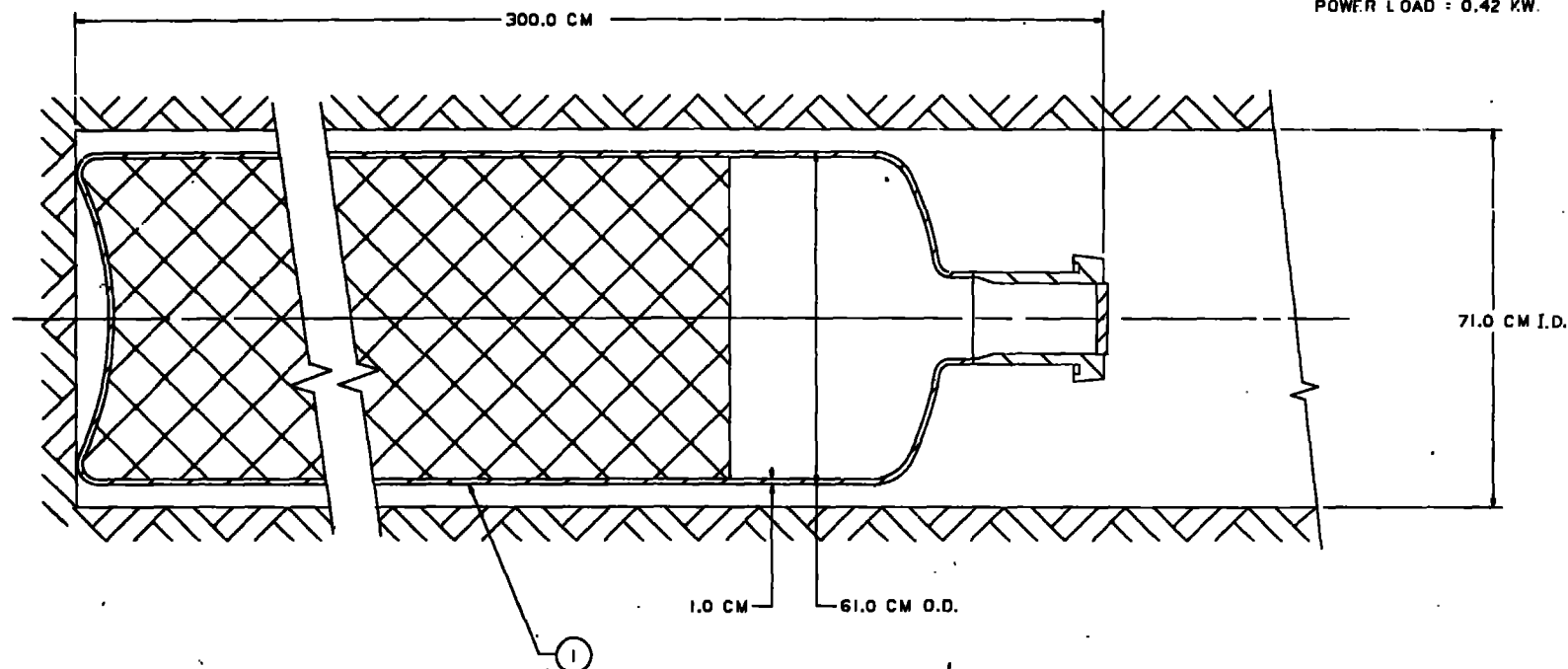
Our desired values for candidate metals properties are summarized in Table 2. These values are meant to serve as general guidelines until detailed design requirements are firmly established.

Corrosion Environment

The waste package/repository environment will include high temperatures, water vapor, atmospheric gases, condensed water containing chemical impurities, and radiation flux. A detailed description of the Topopah Spring unsaturated environment is given in Appendix A. The corrosion environment for the first 1000 years for which the metals were selected is summarized in Tables 3 and 6.

NOTES :

1. CADDS FILE NAME : LNC.WASTE.DRAW 2.
2. DO NOT SCALE DRAWING.
3. WASTE PACKAGE WEIGHT : 4300 LBS. (1950 KGS).
4. TEN YEAR OUT-OF-REACTOR POWER LOAD : 0.42 KW.



REV.	BY	CHK.	DATE	DESCRIPTION
A	JW	Yes		ADDED 71.0 CM I.D.
LET.	DRG.	CHK.	DATE	CHANGE

1		DEFENSE HIGH LEVEL WASTE CANISTER ASSEMBLY		AISI 304 SST.	
ITEM	PART NO.	MATERIAL / DESCRIPTION		REQ'D	ALL STOCK NO.
DR. J. WATKINS		4/25/83		CLASSIFICATION	
CH. C. F. F. F.		7/15/83		MAJOR UNIT NNWSI REPOSITORY	
APPROVED		7/25/83		SUB ASBY. VERT. EMPLACED WASTE PKG.	
SHOWN ON		DATE		DETAIL REF. DHLW WASTE PKG.	
NO. REQ'D PER ASBY.		DATE		REPRODUCTION PROHIBITED WITHOUT PERMISSION OF THE MECHANICAL ENGINEERING DEPARTMENT.	
LAWRENCE LIVERMORE NATIONAL LABORATORY		MECHANICAL ENGINEERING DEPARTMENT		UNIVERSITY OF CALIFORNIA	
J.G.		DRAWING NO.		AAA 83-106352-0A	
COPY		ACCT. NO. 6085-25		SHEET 1 OF 1	

Figure 1. Reference waste package design for DHLW emplaced in vertical borehole.



Figure 2. Reference waste package design for CHLW emplaced in vertical borehole.

Table 1. LLNL design requirements derived from NRC 10 CFR 60.

Waste packages shall be designed to:	
1.	Contain the waste for 300 to 1000 years. ^{a,b}
2.	Maintain a release rate less than 10^{-5} per year of radionuclide inventory present at the end of the containment period (300 years minimum). ^b
3.	Be retrievable for 50 years after emplacement of the first waste package. ^a
4.	Meet nuclear criticality standards, i.e., not exceed an effective multiplication factor (K_{eff}) of 0.95.
5.	Not exceed temperature limits of the waste forms, which are 773 K (500°C) for DHLW glass, 673 K (400°C) for CHLW glass, and 623 K (350°C) for spent fuel cladding.
6.	Not leak radioactive material in excess of applicable federal and state standards after a drop test of two times waste package length onto an unyielding surface, at the minimum anticipated temperature. ^{a,c}
7.	Not leak radioactive material in excess of applicable federal and state standards after sustaining a 1073 K (800°C), 30-minute fire test. ^a
8.	Not leak radioactive material in excess of applicable federal and state standards during or after transportation, handling, emplacement, retrieval, and expected seismic loads. Further, these loads must not compromise long-term performance. ^a
9.	Retain legible, externally labeled identification up to and including retrieval.
10.	Meet federal regulatory requirements for transportation of high level nuclear waste (DHLW and CHLW pour canisters). ^a
11.	Meet requirements with considerations for cost-effectiveness, including direct package costs and related repository system costs through the operational period. ^a

^a These requirements determine or affect the selection of containment barrier metal.

^b Interactions of waste package materials and hole-liner materials must not significantly increase the release rate of the waste forms or the corrosion rate of the containment barriers.

^c With minimum ambient temperatures at Yucca Mountain on the order of -18°C and low waste form power-loads (as low as 50 W), the outer skin temperature of the waste packages is assumed to be -18°C minimum.

Table 2. Screening criteria for candidate metals.

Attribute	Desired value
Corrosion	1 mil (0.0254 mm)/year max
Yield strength at 800°C	10,000 psi (275.5 MPa) min
Impact strength at -18°C	15 ft-lb (20 J) Charpy v-notch, min
Ductility at -18°C	25% elongation, min (annealed)
Weldability	As good as 304L stain- less steel
Total cost (1-cm-thick plate)	\$1/in. ³ (\$0.061/cm ³)

General and local corrosion data were obtained from the available literature and preliminary LLNL corrosion tests. All important known corrosion mechanisms that each metal will be subjected to in the Yucca Mountain repository environment were considered. These are: general and localized corrosion; pitting, crevice, and intergranular corrosion; and stress-assisted corrosion. A detailed discussion of waste package containment barrier corrosion mechanisms is given in Appendix B.

Table 3. Calculated waste package corrosion environment during initial 1000-year period.

Waste package	Duration (years) (based on overpack temperature)			Initial gamma ³ dose rate (rem/hr)
	Steam/Air ($t_{bh} > 100^{\circ}\text{C}$)	Steam/Air ^a ($t_{can} > 100^{\circ}\text{C}$)	Humid air/Water film ($t_{can} < 100^{\circ}\text{C}$)	
DHLW	40	20	940	6.6×10^3
CHLW	110	70	820	1.1×10^3
Spent fuel	770	230	0	1.9×10^4

^a Indicates period when water drips on and flash evaporates from the canister.

^b bh = borehole.

Nomination of Candidate Metals

A list of 17 candidate metals which potentially will meet our design requirements is given in Table 4. These metal alloys are of three types:

- Iron-base alloys with a ferritic structure (numbers 1-4 in Table 4);
- Iron-base to nickel-base alloys with an austenitic structure (numbers 5-13); and
- Copper, titanium, and zirconium-base alloys (numbers 14-17).

The list of metals will be further screened later in this report to yield the five top contenders.

Iron-Base Alloys with a Ferritic Structure

The ferritic metals considered for this group are low-carbon steels, despite the fact that low-carbon steels may have a high corrosion rate in the anticipated oxidizing environment of the repository. The redeeming properties of these steels are: lowest overall unit cost; acceptable strength at room temperature and 800°C; and

Table 4. Candidate metals for canisters and overpacks.

Commercial material designation	ASTM unified numbering system	Chemical composition (wt%)*
1. AISI 1020 cs	UNS G10200	C .18-.23, Mn .3-.6, P .04 max, S .05 max
2. ASTM A537B cs	—	C .24 max, Mn .7-1.35, P .035 max, S .04 max, Si .15-.5, Cr .25 max, Ni .25 max, Mo .08 max, Cu .35 max
3. AISI 409 ss	UNS S40900	C .08 max, Cr 10.5-11.75, Mn 1.0 max, Ni 0.50 max, P .04 max, S .045 max, Si 1.0 max, Ti 6X C min - 0.75 max
4. 26 Cr-1 Mo ss	UNS S44626	C .06 max, Cr 25-.27, Cu .2 max, Mn .4 max, Mo .75-1.50, N .04 max, Ni .05 max, P .04 max, S .02 max, Si .75 max, Ti 0.20-1.00, Other Ti 7X (C+N) min
5. AISI 304L ss	UNS S30403	C 0.030 max, Cr 18.00-20.00, Mn 2.00 max, Ni 8.00-12.00, P 0.045 max, S 0.030 max, Si 1.00 max
6. AISI 321 ss	UNS S32100	C 0.08 max, Cr 17.00-19.00, Mn 2.00 max, Ni 9.00-12.00, P 0.045 max, S 0.030 max, Si 1.00 max, Ti 5X C min
7. AISI 316L ss	UNS S31603	C 0.030 max, Cr 16.00-18.00, Mn 2.00 max, Mo 2.00-3.00, Ni 10.00-14.00, P 0.045 max, S 0.030 max, Si 1.00 max
8. AISI 317L ss	UNS S31703	C 0.030 max, Cr 18.00-20.00, Mn 2.00 max, Mo 3.00-4.00, Ni 11.00-15.00, P 0.045 max, S 0.030 max, Si 1.00 max
9. Nitronic 33 ss	UNS S24000	C 0.08 max, Cr 17.00-19.00, Mn 11.50-14.50, N 0.02-0.40, Ni 2.50-3.75, P 0.060 max, S 0.030 max, Si 1.00 max
10. JS 700 ss	UNS N08700	C .04 max, Ni 24.0-26.0, Cr 19.0-23.0, Mo 4.3-5.0, Nb 6X C min-.04 max, Si 1.0 max, Mn 2.0 max, P .04 max, S .03 max, Cu .5 max
11. Ferralium 255 ss	UNS S32550	C .04 max, Cr 24.0-27.0, Mo 2.0-4.0, Ni 4.5-6.5, Si 1.0 max, Mn 1.5 max, N .10-.25, Cu 1.5-2.5
12. Incoloy 825	UNS N08825	Al 0.2 max, C 0.05 max, Cr 19.5-23.5, Cu 1.5-3.0, Fe bal, Mn 1.0 max, Mo 2.5-3.5, Ni 38.0-46.0, S 0.03 max, Si 0.5 max, Ti 0.6-1.2
13. Inconel 625	UNS N06625	Al 0.40 max, C 0.10 max, Nb 3.15-4.15, Cr 20.0-23.0, Fe 5.0 max, Mn 0.50 max, Mo 8.0-10.0, Ni bal, P 0.015 max, S 0.015 max, Si 0.50 max, Ti 0.40 max
14. Ti Grade 2	UNS R50400	C 0.10 max, H 0.015 max, Fe 0.30 max, N 0.03 max, O 0.25 max, Ti Rem
15. Ti Grade 12	—	N .03 max, C .08 max, H .015 max, Fe .3 max, O .25 max, Mo .2-.4, Ni .6-.9, Ti Rem
16. Zr 702	UNS R60702	C 0.05 max, H 0.005 max, Hf 4.5 max, N 0.025 max, Other Zr + Hf 99.2 min, Fe + Cr 0.2 max
17. Cupronickel 70/30	UNS C71590	Al 0.002 max, As 0.001 max, Bi 0.001 max, C 0.03 max, Co 0.05 max, Cu 67.0 min, Hg 0.0005 max, Fe 0.005 max, Mn 0.001 max, Ni 29.0-33.0, P 0.001 max, Pb 0.001 max, S 0.003 max, Sb 0.001 max, Si 0.02 max, Sn 0.001 max, Ti 0.001 max, Zn 0.001 max, Other Ag included in Cu, Co included in Ni, Cu + all named elements 99.5 min

* References 4 through 7.

good weldability. The two low-carbon steels that we considered are AISI 1020 and ASTM A537B. Carbon steel is the reference metal for horizontal borehole liners, based on its low cost and projected survival during the retrieval period.

Alloying carbon steels with chromium and molybdenum increases the corrosion resistance under oxidizing conditions. The ferritic alloy steels under consideration are expected to resist attack by pitting and crevice corrosion as well as stress-corrosion cracking. The shortcomings of this group are low fracture toughness values and poor weldability. The ferritic alloy steels considered are AISI 409 Ti stabilized stainless steel and 26 Cr-1 Mo stainless steel.

Iron-Base to Nickel-Base Alloys with an Austenitic Structure

The NNWSI reference canister and overpack metal, which also is the reference for the DHLW and CHLW pour-canisters, is AISI 304L stainless steel. The engineering properties of 304L stainless steel rate very well, with the exception of susceptibility to localized corrosion and to stress-corrosion cracking. If intergranular stress-corrosion cracking is excessive for 304L stainless steel in the Topopah Spring environment, other stabilized austenitic stainless steels such as 321 stainless steel, or nickel-base alloys, such as Incoloy 825, are appropriate choices. If transgranular stress-corrosion cracking is a prob-

lem for the austenitic stainless steels, an alloy with greater than 20% nickel content,^{8,9} such as Incoloy 825, is appropriate.

If pitting and/or crevice corrosion attack is excessive in 304L stainless steel, then an alloy with increased molybdenum, e.g., AISI 316L and AISI 317L stainless steels, or Incoloy 825, will increase the resistance to these forms of corrosion. All of the 300 series stainless steels may be specified with the extra-low carbon (0.02 max) modification to avoid sensitization in the high-temperature glass-pouring process, and in the final top-cap weld on canister and overpacks.

Copper, Titanium, and Zirconium-Base Alloys

The titanium alloys are expected to be very resistant to conditions that may occur in a strong field of gamma radiation. These alloys are also very resistant to localized forms of corrosion, but lose most of their mechanical strength at 800°C. When compared to the other metals, cupronickel 70/30 has competitive strength and weldability properties, but is vulnerable to corrosion by nitric acid and other oxidizing species in a radiolyzed air-water environment. Zirconium alloys have proven performance in aqueous, radiolyzed environments, but exhibit low mechanical strengths at 800°C, as well as marginal fracture toughness values at -18°C, and are the most costly of the candidate metals considered.

Metals Data

A summary of all of the metals data obtained is presented in Tables 5, 7, 8 and 9. All references used to obtain these data are listed in Appendix C.

Corrosion Data

The corrosion data presented in Table 5 were assembled utilizing literature data and judgment based upon experience. These data were used to rank the candidate materials and subsequently select the top contenders. These data are presented in commonly used units of mils per year and are for unirradiated conditions. The estimated probability factors shown represent an attempt to rank the corrosion mechanisms according to their estimated relative contributions toward producing ul-

timate failure in the repository environment for each candidate metal. These estimates are believed to be conservative, but are not meant to be applied as design data for dimensioning canister and overpack wall thicknesses for corrosion allowance.

There is abundant evidence in the literature,¹⁰ dating back as early as 1910, that when moist air is irradiated with ionizing radiation, nitric acid will form. In radiation corrosion experiments with moist air,¹¹⁻¹⁴ it has generally been found that metals known to be vulnerable to corrosion by nitric acid also corrode in irradiated, moist air. It is difficult to estimate accurately the increase in corrosion rates due to irradiation. For conditions in the tuff repository, the relative increases in corrosion rates would probably be significant for

Table 5. Estimated relative maximum corrosion rates for selection of candidate metals.^a (See Table 3 for reference corrosion environment.)

Material designation or composition	Steam (mpy)	Moist air condition (mpy)	Continuous air/water film								Stress corrosion cracking					
			Corrosion mechanisms, rates (mils/yr), ^b probabilities								Intergran.		Transgran		H ₂ embrit.	
			General		Pitting		Crevice		Intergran.		Rate	Prob.	Rate	Prob.	Rate	Prob.
AISI 1020 steel	0.05	2	8	0.2	30	0.5	40	0.3								
A537 steel	0.05	2	8	0.2	30	0.5	40	0.3								
409 st. steel	0.02	0.1	0.8	0.55	5	0.3	25	0.1							80	0.05
26 Cr-1 Mo steel	0.02	nil	0.04	0.6	10	0.05	10	0.15	40	0.05	40	0.05			80	0.15
304L st. steel	0.02	nil	0.04	0.2	30	0.15	40	0.3	60	0.15	60	0.15	100	0.05		
321 st. steel	0.02	nil	0.04	0.2	30	0.15	40	0.3	30	0.15	30	0.15	100	0.05		
316L st. steel	0.02	nil	0.04	0.3	10	0.1	15	0.25	60	0.15	60	0.15	100	0.05		
317L st. steel	0.02	nil	0.04	0.4	5	0.05	8	0.20	60	0.15	60	0.15	100	0.05		
Nitronic 33	0.02	nil	0.04	0.2	30	0.15	40	0.3	60	0.15	40	0.15	100	0.05		
JS 700	0.02	nil	0.04	0.2	3	0.15	6	0.3	40	0.15	40	0.15	30	0.05		
Ferralium 255	0.02	nil	0.04	0.3	10	0.1	15	0.25	50	0.15	50	0.10	100	0.05	80	0.05
Incoloy 825	0.02	nil	0.04	0.6	2	0.1	4	0.15	30	0.05	30	0.05	100	0.05		
Inconel 625	0.02	nil	0.04	0.7	1	0.1	2	0.1	30	0.05	30	0.05				
Ti Code 2	0.02	nil	0.04	0.8	1	0.05	2	0.05							200	0.1
Ti Code 12	0.02	nil	0.04	0.8	0.2	0.05	0.5	0.05							200	0.1
Zr 702	0.02	nil	0.04	0.8	0.2	0.05	0.5	0.05							200	0.1
Cu-Ni 30	0.02	0.06	0.2	0.3	0.6	0.3	1.6	0.3	20 ^c	0.1 ^c						

^a Data not to be used for prediction of corrosion rates.

^b To convert mils/yr to $\mu\text{m/yr}$, multiply by 25.4.

^c Dealloying phenomenon.

Table 6. Underground environments.

	Topopah Spring ³ tuff	Chino silt loam ¹⁵ (14-yr data)
Chemical concentrations of water extract (ppm)	SiO ₂ -61.0, Na-51.0, K-4.9, Ba-.003, Ca-14.0, Mg-2.1, Fe-0.04, Al-0.03, F-2.2, Cl-7.5, NO ₃ -5.6, SO ₄ -22.0, Li-0.05, Sr-0.05, PO ₄ -0.12, HCO ₃ -120.0	Na + K-76.5, Ca-124, Mg-22, HCO ₃ -13, Cl-60.5, SO ₄ -169
Water	8 mm/yr (net)	386 mm/yr (average rainfall furnished by the US Weather Bureau)
Resistivity	high	low
pH	~neutral	~neutral
Redox	oxidizing	oxidizing
Air-pore space	17%	16%
Moisture percentage	14%	26%
Internal Drainage	good	good
Atmosphere	air-water/film-steam	air-water/film
Temperature	29-250°C	10°C-28°C ¹⁸
Radiation field	gamma (CHLW), 1.1 × 10 ⁵ rem/hr max	background
Areal thermal loading	50 kW/acre (initial)	solar
Corrosion products	scale	scale
Pitting Corrosion Data		
AISI 304 s. stl.	TBD (to be determined)	1.1 mpy (28 μm/yr)
AISI 316 s. stl.	TBD	4 × 10 ⁻⁵ mpy (10 ⁻³ μm/yr)
AISI 430 s. stl.	TBD	4.4 mpy (112 μm/yr)
AISI 410 s. stl.	TBD	4.4 mpy (112 μm/yr)

Table 7. Estimated costs of candidate metals.

Material	Raw material cost (plate) (\$/in. ³) ^a	Manufacturing cost for 1/2-in. wall-welded pipe (\$/in. ³) ^a	Total cost (\$/in. ³)
AISI 1020 steel	0.1	0.2	0.3
A537 steel	0.1	0.2	0.3
409 Ti stabil. st. steel	0.3	0.3	0.6
26 Cr-1 Mo steel	1.1	0.3	1.4
304L st. steel	0.4	0.2	0.6
321 st. steel	0.5	0.2	0.7
316L st. steel	0.5	0.2	0.7
317L st. steel	0.6	0.2	0.8
Nitronic 33 st. steel	0.4	0.2	0.6
JS 700 st. steel	1.0	0.3	1.3
Ferralium 255 st. steel	0.7	0.5	1.2
Incoloy 825	1.2	0.5	1.7
Inconel 625	2.6	0.5	3.1
Ti Code 2	1.6	0.5	2.1
Ti Code 12	1.8	0.5	2.3
Zr 702	3.5	0.6	4.1
CDA 715 (copper-nickel 70/30)	1.0	0.4	1.4

^a To convert \$/in.³ to \$/cm³, multiply by 6.1 × 10⁻².

Table 8. Mechanical properties of candidate metals.

Material	Tensile strength (ksi) ^a	Yield strength at 800°C (ksi) ^a	Elongation (%) minimum static	Nil ductility temperature (°C) for 1/2-in.-thick plate	Fracture toughness minimum at -18°C	
					(ft-lb) ^b	(ksi-in. ^{1/2}) ^c
AISI 1020 steel	60	8	30	-18	8	-
A537 steel	80	8	22	-30	40	107
409 Ti stabil. st. steel	70	5	25	-29	20	-
26 Cr-1 Mo steel	70	7	20	-18	20	-
304L st. steel	80	12	40	< -148	100	142
321 st. steel	85	13	40	< -148	90	129
316L st. steel	80	13	40	< -148	110	150
317L st. steel	80	18	40	< -148	100	156
Nitronic 33	115	20	40	< -148	43	123
JS 700	85	19	40	< -148	100	147
Ferrallium 255	124	25	25	-18	100	-
Incoloy 825	95	23	30	< -148	78	150
Inconel 625	135	45	40	< -148	44	130
Ti Code 2	50	1	21	< -148	30	65
Ti Code 12	70	3	18	-18	11	35
Zr 702	55	1	16	-18	11	35
CDA 715 (copper-nickel 70/30)	44	17	37	< -148	113	-

^a To convert ksi to MPa, multiply by 6.9.

^b To convert ft-lb to joules, multiply by 1.36.

^c To convert ksi-in.^{1/2} to MPA-m^{1/2}, multiply by 0.18.

Table 9. Weldability parameters for candidate metals.^a

Material designation or composition	Preheat	Special interpass temp.	Post-heat treat	Special atm.	Low weld, HAZ ^b toughness	Non-standard process	Non-standard NDE	Non-econ. rel. to AISI 304	Special fit-up
AISI 1020 steel	0	0	0	0	0	0	0	0	0
A537 steel	0	1	0	0	0	0	0	0	0
409 Ti stabil. st. steel	1	1	1	0	1	0	0	1	0
26 Cr-1 Mo st. steel	0	0	1	1	1	0	0	1	1
304L st. steel	0	0	0	0	0	0	0	0	0
321 st. steel	0	0	0	0	0	0	0	0	0
316L st. steel	0	0	0	0	0	0	0	0	0
317L st. steel	0	0	0	0	0	0	0	1	0
Nitronic 33 st. steel	0	0	0	0	0	0	0	1	0
JS 700 st. steel	1	1	1	0	0	0	0	1	1
Ferrallium 255 st. steel	0	1	0	0	0	0	0	0	1
Incoloy 825	0	0	0	0	0	0	0	1	1
Inconel 625	0	0	0	0	0	0	0	1	1
Ti Code 2	0	0	0	1	0	0	0	1	1
Ti Code 12	0	0	0	1	1	0	1	1	1
Zr 702	0	0	0	1	1	0	0	1	1
CDA 715 (copper-nickel 70/30)	0	1	0	0	0	0	0	1	1

^a Yes (1) or no (0) special problems.

^b Heat-affected zone.

copper-based alloys. Makepeace¹⁴ reported a 6-month irradiation experiment which indicated that certain austenitic stainless steels and nickel-base alloys had very low corrosion rates in moist air irradiated with a gamma-ray flux of 5 to 6 megarads per hour at ambient temperature. Under the same conditions, copper samples showed higher corrosion rates. Although this experiment was carried out at a higher dose rate, a lower temperature, and for much shorter times than are of interest for the tuff repository, the results are indicative of the type of corrosion behavior to be expected under irradiation conditions.

Presently no long-term underground corrosion data exist for our candidate metals in an environment exactly like that at Yucca Mountain¹⁷ (see Appendix A for a detailed description of the Yucca Mountain corrosion environment). However, underground corrosion data for a few of the candidate metals were found for Chino silt loam for a 14-year test.¹⁵ Table 6 lists the significant attributes of both environments and presents available data. Figure 4 compares the two environments schematically. The data presented in Table 6 indicate the following for the Chino silt loam environment:

- A Mo-containing austenitic stainless steel (e.g., type 316) performed better than an ordinary Ni-Cr austenitic stainless steel (e.g., type 304).

- Ferritic stainless steels (e.g., types 430 and 410) did not perform as well as 304 stainless steel.

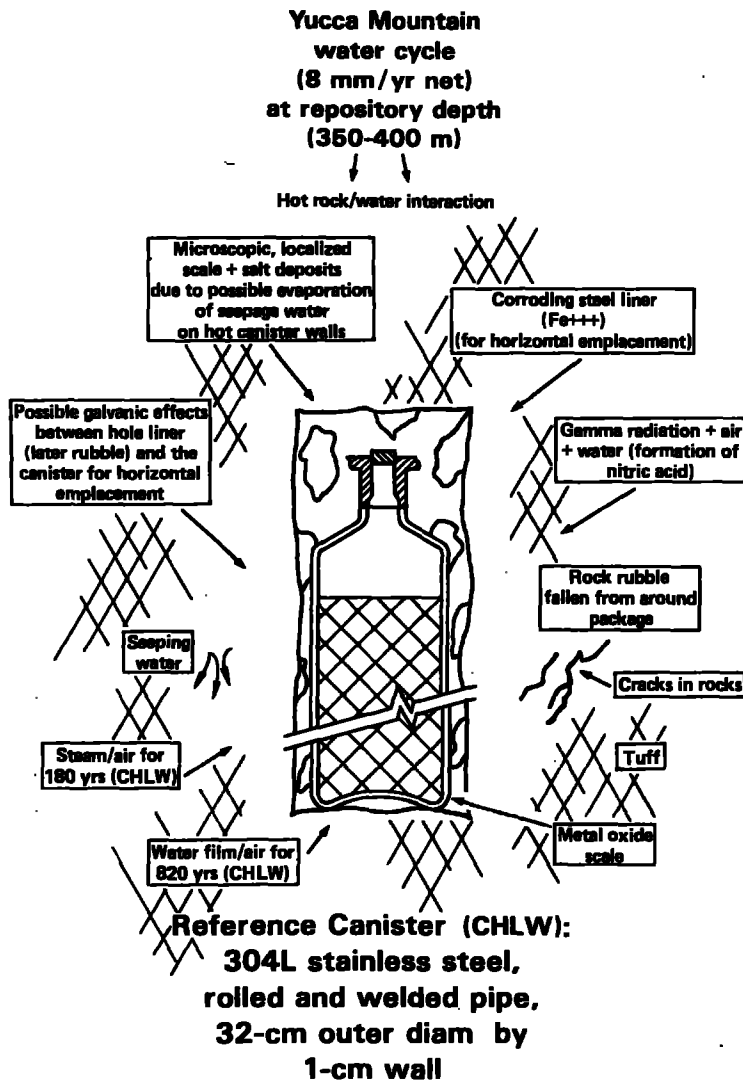
Performance was determined by general corrosion and pitting corrosion rates on coupons of these alloys buried in soil. Relationships between the corrosivity of soils and factors such as soil resistivity, pH, aeration, and the corrosion products formed have been suggested in the literature.^{15,16}

Although major differences are shown between the Chino silt loam environment and the Topopah Spring tuff of Yucca Mountain environment, there are also some similarities, and these data represent "best guesses" for long-term underground conditions until site-specific data for the repository environment become available.

Material and Fabrication Costs

Rolled and welded pipe manufacturing processes are representative of the kind of fabrication involved in manufacturing overpacks. Diameters

**Topopah Spring Tuff
Environment,
1000-year exposure,
Corrosion rate under investigation.**



**Chino Silt
Loam Environment,
14-year exposure,
Corrosion rate ~ $10^{-3} \mu\text{m/yr}$ (316SS).**

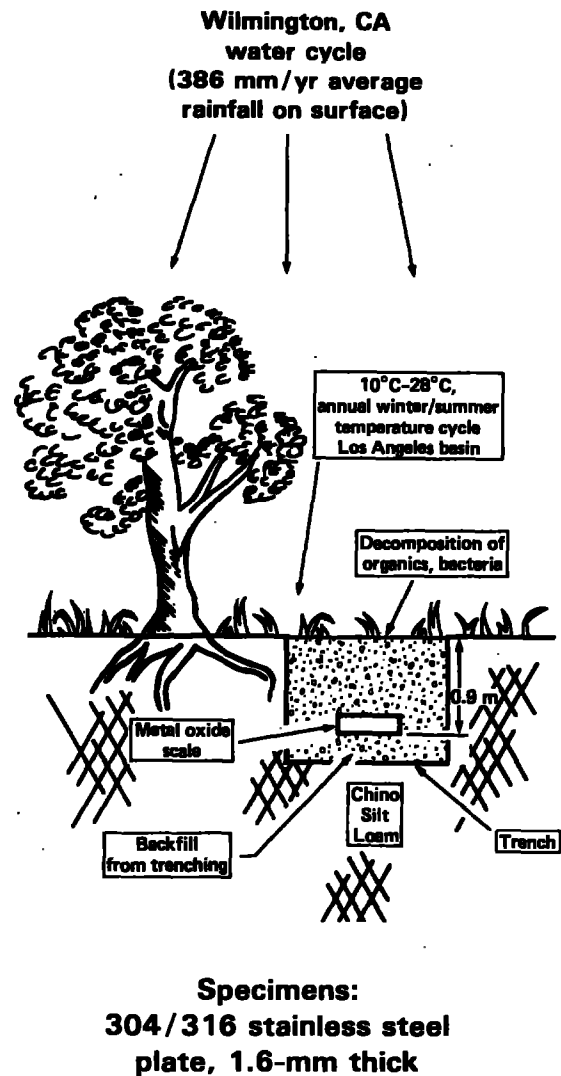


Figure 4. Comparison of underground corrosion environments.

of 0.3 to 0.91 m represent the upper limit of canister and overpack diameters that we contemplate in our designs, so we used the cost of 0.91-m (36-in.) diam by 12.7-mm (1/2-in.) wall, welded pipe as a measure. These costs were obtained by telephone contact with commercial fabricators. The costs of alternative fabrication processes such as extrusion and centrifugal casting were also considered, but were rejected due to high cost or failure to meet our minimum design requirements. Table 7 shows the costs of the candidate metals.

Desired Mechanical Properties

Certain mechanical properties are important in this application: fracture toughness at 255 K (-18°C), elongation, nil-ductility temperature, tensile strength, and yield strength at 1073 K (800°C). Fracture toughness at lowest ambient temperature is a property of a material that defines its resistance to brittle fracture. This property is dictated by the requirement that the waste package survive a drop test from a height of two

times the package length without leaking. During transportation and at Yucca Mountain, minimum handling temperatures are roughly 255 K (-18°C). The ductility (elongation) is also important to the drop test requirement. The fracture toughness of certain alloys exhibits significant variations with changes in temperature. The nil-ductility temperature is that temperature below which normally ductile materials behave in a brittle fashion.

The ultimate tensile strength is a measure of the stress which will lead to fracture of the material. The margin between the yield strength and the ultimate strength is a measure of the degree to which stretching and bending rather than fracture takes place after the yield strength is exceeded. Actual designs will load the material to a stress below the yield strength, including a factor of safety. The yield strength at 1073 K (800°C) is related to high temperature glass pouring operations and to the requirement of surviving a 1073 K (800°C), 30-minute fire test without leaking. Table 8 summarizes the mechanical properties data.

Weldability

The waste package containment barrier will have several welded joints. The final weld of the

top-cap to the main overpack and canister bodies will be done remotely. Table 9 lists the weldability data. Possible welding problems were identified by yes (1) or no (0) binary evaluation of the following characteristics: preheat requirements, special interpass temperature, postheat requirements, special welding atmosphere, low weld toughness, nonstandard welding process, nonstandard non-destructive evaluation process, special cleanliness during fit-up, and not economical relative to 304 stainless steel. The overall weldability also includes all dimensional and mechanical property requirements of the weld and heat-affected zone.

Extensive discussions on weldability were held with H. Weiss, P. Landon, C. Witherell, all LLNL; J. Lippold, Sandia National Laboratories; and metals suppliers and pipe fabricators.

Ranking of Candidate Metals

The 17 candidates have been ranked according to the data shown in Tables 5, 7, 8, and 9. Each factor (corrosion resistance, cost, mechanical properties, and weldability) was given the same weighting. A score of 0 was designated for "some disadvantages", 1 for "suitable" and 2 for "superior." Table 10 shows the results.

Table 10. Ranking summary for candidate metals.

Material designation	Corrosion resistance ^a	Mechanical properties ^a	Weldability ^a	Cost ^a	Score	Rank ^b
AISI 1020 steel	0	1	2	2	5	3
A537 steel	0	2	1	2	5	3
409 st. steel	1	1	1	1	4	3
26 Cr-1 Mo steel	1	1	0	0	2	3
304L st. steel	1	2	2	2	7	1
321 st. steel	1	2	2	2	7	1
316L st. steel	1	2	2	2	7	1
317L st. steel	1	2	2	1	6	2
Nitronic 33	1	2	2	1	6	2
JS 700	2	2	0	1	5	3
Ferralium 255	1	2	1	1	5	3
Incoloy 825	2	2	2	1	7	1
Inconel 625	2	2	2	0	6	2
Ti Code 2	2	0	1	0	3	3
Ti Code 12	2	0	0	0	2	3
Zr 702	2	0	0	0	2	3
Cu-Ni 70/30	0	2	1	1	4	3

^a 0 = some disadvantages, 1 = suitable, 2 = superior.

^b 1 = highest, 3 = lowest.

Results and Recommendations

Analysis of the data presented in this report resulted in selection of the four highest ranking metals out of the 17 candidates for canisters or overpacks. AISI 1020 carbon steel was chosen for hole liners. Summary statements are given on these metals.

AISI 304L Stainless Steel: a low carbon, general-purpose austenitic stainless steel. We will further specify a premium grade with an extra low carbon content of less than 0.02% C if experimental results and analysis indicate that chromium carbide precipitation (sensitization) will occur during welding and glass pouring.

AISI 321 Stainless Steel: a general-purpose, austenitic stainless steel with a titanium addition for stabilization of the carbon, thus preventing the formation of chromium-carbides (sensitization) during welding and glass pouring, as well as over long periods of time, at low temperatures (100–300°C).

AISI 316L Stainless Steel: a low carbon, austenitic stainless steel with the addition of 2–3% molybdenum for more resistance to pitting corrosion than type 304L. We will further specify a premium grade with an extra low carbon content of less than 0.02% C if experimental results and analysis indicate that chromium carbide precipitation (sensitization) will occur during welding and glass pouring.

Incoloy 825: a nickel-iron-chromium-molybdenum-copper austenitic alloy designed for use in extremely corrosive environments. This alloy is stabilized with titanium to resist intergranular corrosion and intergranular stress corrosion cracking. The nickel content makes it very resistant to transgranular stress corrosion cracking. The molybdenum and copper give this alloy resistance to pitting and crevice corrosion. The high chromium content gives it resistance to various types of oxidizing environments.

AISI 1020 Steel: a low carbon, general-purpose steel, for horizontal borehole liners, appropriate for a 50-year retrieval period. AISI 1020 steel has satisfactory properties for use as hole liners and is very attractive from a cost standpoint.

The remaining materials were not selected for the following reasons:

- ASTM A537B steel: low corrosion resistance for overpacks and canisters, and more expensive compared to AISI 1020 steel for horizontal borehole liners.

- AISI 409 stainless steel: relative weldability problems.

- 26 Cr-1 Mo steel: relative weldability problems.

- AISI 317L stainless steel: more expensive compared to AISI 316L stainless steel, with limited improvement in corrosion resistance.

- Nitronic 33: more expensive compared to AISI 304L stainless steel, with minor improvement in properties.

- JS 700: more expensive compared to AISI 304L stainless steel and weldability problems.

- Ferralium 255: unacceptable nil-ductility temperature and more expensive than AISI 304L stainless steel.

- Inconel 625: more expensive than Incoloy 825.

- Ti Code 2: expensive, low yield strength at 800°C.

- Ti Code 12: expensive, relative weldability problems, low fracture toughness.

- Zr 702: expensive, relative weldability problems, low fracture toughness.

- Cupronickel 70/30: low corrosion resistance in gamma-irradiated moist air and aerated water.

Conclusion

The results of our analysis show the five metals that best satisfy the requirements for disposal of high-level waste at the NNWSI-proposed repository at Yucca Mountain. Testing is presently planned or in progress on these metals for further development of the waste package design for the unsaturated zone. The reference canister and overpack metal is AISI 304L stainless steel, but

alternative metals will also be considered for reasons previously discussed. The primary alternative metals have been selected from the list of the 17 candidate metals discussed in this report. They are AISI 321, AISI 316L, Incoloy 825 for canisters and overpacks, and 1020 carbon steel for borehole liners.

Acknowledgment

The authors wish to express appreciation to Dr. Richard Van Konyenburg for his thorough review of this report.

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Appendix A. Emplacement Environment

The NNWSI project has selected the Topopah Spring Member of the Paintbrush Tuff as the repository target horizon for a repository sited at Yucca Mountain. The repository will be located in a welded portion of the tuff unit and will lie approximately 350 to 400 meters below surface level. The static water level is over 100 meters below the repository level. The depths given here are based on information obtained from geologic and hydrologic boreholes around the edge of the repository block and from the principal borehole (USW G-4) at the exploratory shaft. The exact depth of the repository horizon will be established during the exploratory shaft phase of the program.

The choice of the unsaturated zone marks a departure from the conventional environment in which repository siting has been proposed. There are many characteristics of the unsaturated zone which make use of this regime particularly attractive for a high-level waste repository site. Several advantages of the unsaturated zone over the saturated zone are described below:

- The waste canisters will not be submerged in a continuum of water. Rather, they will be subjected to constant contact with water vapor and to intermittent contact with limited amounts of liquid water.
- The pressure exerted on the canisters by the environment will be approximately 1 atmosphere. There is no hydrostatic pressure because there is not a continuum of water above or around the canisters.
- The environment to which the canister is exposed will be of air plus water vapor, if the temperature is more than 100°C.* This is a consequence of the absence of hydrostatic pressure.
- Aqueous corrosion of the canister or overpack can only begin after the temperature has dropped to less than 100°C. This is because liquid water cannot exist in the unsaturated zone at temperatures higher than 100°C, the 1-atmosphere boiling point of water. Calculations of thermal history for reference canisters show that for CHLW, canister temperatures will drop below 100°C approximately 180 years after waste emplacement. For spent fuel packages, the canister temperature will remain 100°C or greater for approximately 1000 years after emplacement (see Table 3).
- The vadose water and atmosphere of the repository will be mildly oxidizing. This may promote the growth of a protective coating of oxidation products on the skin of metal components of the waste package. Such oxidized coatings can form protective layers against further corrosion, as in the cases of stainless steel, zirconium, and titanium.
- Water available for corrosion and waste form dissolution is limited to the small amount supplied by downward infiltration from the overlying unsaturated media, a flux currently estimated to be about 8 mm/year.
- It may be possible to design the repository so that the limited amount of water which enters the repository area drains through the area by fracture flow. This would result in reduced contact time for water, waste canister, and waste form, a factor which would reduce radionuclide release to very low levels.
- The low pressure in the repository means that canisters and overpacks do not need to be designed to withstand high hydrostatic pressures. The only strength requirements for canisters and overpacks will be that they must withstand any stress conditions which might arise during normal and accident handling and emplacement operations, or during retrieval operations and expected seismic events.

* The actual boiling point of water at the repository horizon will be about 95°C; for simplicity in reading, 100°C is used throughout this discussion.

Appendix B

Metal Components for Use as Canister and/or Overpack Materials

The reference metal for use in overpack and canister fabrication for the NNWSI repository is 304L stainless steel. In this section, we will provide an upper-limit estimate for the rate of uniform corrosion of this material in the unsaturated zone. We will then describe a research and development program to determine the actual rate of uniform corrosion under expected repository conditions and whether any nonuniform corrosion mechanisms can be expected to be important.

The maximum calculated consumption of 304L stainless steel by uniform corrosion in Topopah Spring tuff has been calculated to be 0.12 cm in the first 1,000 years after waste emplacement (see following discussions). This estimate was calculated using the thermal history for CHLW and DHLW canisters, which require a larger corrosion allowance than spent-fuel canisters. The spent-fuel corrosion allowance can be less because the canister will remain free from contact with liquid water for 770 years after emplacement (see Table 3) (for the period from 770–1000 years, water contacting the 100°C canister will flash evaporate).

Corrosion rates were estimated for 304L stainless under three corrosion regimes. In all cases, the most conservative estimates allowed by the existing data were used. The basis for the estimates is discussed. The data used were taken from results on types 302, 304, and 304L, which differ primarily in their maximum carbon contents (0.15, 0.08, and 0.03 percent, respectively). The carbon content at this low level should not significantly affect the rate of uniform corrosion. The environments defined and the corrosion rates used are as follows:

- Steam, 300 to 100°C, 0.3 $\mu\text{m}/\text{yr}$.
- Moist air, 100°C, 1.0 $\mu\text{m}/\text{yr}$.
- Hot aerated water, 80 to 100°C, 2.5 $\mu\text{m}/\text{yr}$.

To allow some credit for the actual unsaturated conditions, the steel is presumed to be in contact with water for only half the time period when the temperature is below 100°C.

The corrosion-oxidation rate in steam above 100°C was based on extrapolation of data from higher temperatures down to the repository temperature range. A 2-year test at approximately 600°C in steam indicated a corrosion rate of less than 5 $\mu\text{m}/\text{yr}$ for 304L stainless steel.¹ The corrosion attack was uniform. Data obtained for type 302 at 875°C in "wet" and "dry" air showed rates of 11 and 7.5 $\mu\text{m}/\text{yr}$, respectively, after 300 hours. The rate then slowed to 9 and 4.5 $\mu\text{m}/\text{yr}$, respectively, after 500 hours.¹ The thickness of metal oxidized versus time follows a parabolic rate law so that estimates of consumption based on a linear extrapolation as done here are conservative. Stainless steels show a threshold temperature above which the oxidation rate becomes "appreciable." For the stainless steels considered here, the threshold temperature is about 900°C. In extrapolating the available data to the temperature range of interest for the repository by an Arrhenius rate law, the oxidation rate in wet air becomes essentially zero. However, to assign a nonzero number to the rate, the value of 0.3 $\mu\text{m}/\text{yr}$ was selected based on the sensitivity of the experimental observations and considering the time period over which the observations were made. This value is very conservative and would not be dependent upon the actual temperature at the canister or overpack surface.

Corrosion during the period when water reenters the waste package environment (below 100°C) was estimated by using the corrosion rate at the boiling point of water. The value of 1 $\mu\text{m}/\text{yr}$ was assigned based on atmospheric corrosion of stainless steel type 304. Five-year exposure data at an industrial site in the United Kingdom yielded a rate of 0.12 $\mu\text{m}/\text{yr}$ averaged over the 5-year period. During this time the atmosphere was partially controlled by the use of air pollution controls.² This, again, is a conservative estimate since the industrial environment contains SO_2 that would hydrolyze to give acidic conditions on the metal surface. Because these data were obtained at an assumed prevailing temperature of about 15°C, they were extrapolated to 100°C by assuming that the corrosion rate roughly doubles for each 30°C increase in temperature.³ This assumes that there is no change in the corrosion mechanism.

The corrosion rate for the bulk of a 1,000-year postemplacement period was estimated using the rate for stainless steel immersed in water which is saturated with air in the temperature range of 80 to 100°C. To allow some credit for unsaturated conditions, the canister or overpack was assumed to be immersed only half the time. Again, the assumptions involved here are very conservative. The actual conditions will involve far less water. The corrosion rate which prevails under the immersed conditions is 2.5 $\mu\text{m}/\text{yr}$. This

value was based on a compilation of sources.^{1,4} Three-year data from exposure to Mississippi River water indicated a corrosion rate for 304 of less than 2.5 $\mu\text{m}/\text{yr}$. The same general corrosion rate was obtained for polluted acid mine runoff in Monongahela River water and for more saline Savannah River water (1,300 ppm chloride). In the last case, the metal showed signs of the onset of crevice attack. Experience in boilers and with the high-purity water used in nuclear reactors shows that 304 stainless steel has negligible corrosion rates under those conditions. For example, at 260°C in high-purity water the rate is 1 $\mu\text{m}/\text{yr}$, including the effects of other corrosion attack due to reactor operation. Expected general corrosion rates of 304L stainless steel exposed to water typical of a repository in the unsaturated tuff are low, if the conditions described in Appendix A are correct. A general corrosion rate was assigned for this period and temperature range equal to the highest value in the range recorded from the foregoing references. This estimate will be modified as soon as results are available from the experimental program to be outlined.

The materials testing program for metal components of the waste package will focus on the 300-series austenitic stainless steels. Analysis of the data available on corrosion in a variety of environments shows that several different types of nonuniform corrosion mechanisms are of possible concern if the glass-pour canister is used as the primary containment barrier. The potential problem areas are sensitizing of the steel from the temperatures encountered during glass casting operations, pitting and crevice attack, transgranular stress corrosion, and long-term phase stability of the metal. The following paragraphs discuss the conditions under which it is expected that these factors will be of concern, and the remedies available if 304L shows a nonuniform corrosion mechanism that would rule out its use as the containment barrier. Finally, an outline of the testing program is given. The program is designed to determine the corrosion rate and mechanism for the reference canister material and alternative materials under expected repository conditions.

During the manufacture of waste glass, hot liquid is poured into the canister. The canister wall is exposed to molten glass which has a temperature on the order of 1,100°C at the start of the pouring operation. The canister becomes heated by the glass and cools slowly as the glass cools to room temperature. The relatively low thermal conductivity of the glass (average of 1 W/mK) means that the canister cools slowly through a wide temperature range. The slow cooling allows diffusion of Cr out of the alloy and precipitation of chromium carbides at grain boundaries. The lower the carbon content of the steel, the longer the material must be held at the high temperature for this process to occur. Figure B-1 illustrates this point. The areas to the right of the curves and enclosed by the curves are the time-temperature regions where sensitizing of the steel will occur due to chromium carbide precipitation. Following precipitation, the region surrounding the grain boundaries is Cr-depleted and is likely to corrode at a more rapid rate than the normal alloy. The exact time-temperature history for 304L pour canisters is not presently known; however, when combined with reasonable glass production and cooling scenarios, the curves shown in Fig. B-1 suggest that sensitizing during glass casting should not be a problem.

The curves in Fig. B-1 are for unstressed material. Tensile stress shifts the curves to shorter times at temperature so that these curves cannot be used to accurately predict the time-temperature regime to

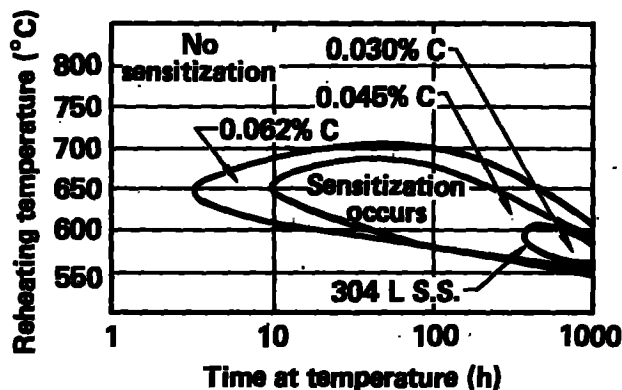


Figure B-1. Temperature-time-sensitization diagram for type 304 stainless steel (modified from Shrier, 1976²²).

cause sensitizing of 304L stainless steel. This question will have to be addressed as part of the materials testing program.

The low-temperature (100 to 300°C) time-temperature sensitizing curves for very long times (hundreds of years) are not known. The potential for sensitizing of 304L in the repository environment will need to be assessed as part of the research and development program.

Other processes that might cause sensitizing of the steel are those associated with welding operations and residual stress from canister fabrication. Any stresses induced before using the canister as the receptacle for hot glass can be removed by annealing the fabricated canister.

If sensitizing of the 304L is shown to occur during glass-casting operations, two alternatives are available: canisters could be overpacked with 304L that was not sensitized; or a different material (such as the stabilized grades of stainless steel 321 or 347), which is not susceptible to chromium carbide formation, could be used for the canister.

If sensitizing is a problem because of the repository cooling history, the solution would be to use a material that would not be sensitized. Preliminary estimates suggest that use of 321 or 347 stabilized grades of steel would eliminate the sensitizing concern and would not introduce new difficulties. Some care needs to be taken when welding these grades of steel; preliminary assessments indicate that the welding method proposed for the Defense Waste Processing Facility (DWPF) should be adequate.

Another possibility for minimizing sensitization effects is use of a premium grade of 304L with carefully controlled extra-low carbon content. As illustrated in Fig. B-1, lowering the carbon content pushes the time-temperature sensitization curves toward the right. The lower carbon content requires longer times before a sensitized structure occurs. In addition, the nitrogen content can be controlled to low levels, because this element also influences the sensitization behavior of stainless steels.

Pitting and crevice attack are a potential concern in the repository environment. These corrosion mechanisms come into play when a concentrated electrolyte comes in contact with a metal susceptible to pitting or crevice corrosion. Chloride concentrations that cause pitting and crevice attack on 304 stainless steel are shown in Fig. B-2. Once these mechanisms of corrosion are initiated, further rapid corrosion can occur at the site of initiation because of the local production of concentrated electrolyte solutions. While normal conditions in a repository sited in the unsaturated zone at Yucca Mountain will not produce solutions with high concentrations of electrolytes, there are some mechanisms by which localized attack by such solutions might occur. For example, water dripping from a fracture onto a hot canister might evaporate, leaving a residue of salts. An accumulation of small amounts of salts in a small area might later produce the potential for pitting or crevice corrosion at that site.

To address this concern, the metals testing program will evaluate the susceptibility of 304L stainless steel to pitting and crevice corrosion under "over-stress" conditions of concentrated electrolyte solutions containing ions known to be present in water at the repository level. Particular emphasis will be placed on chloride and fluoride ions that are known to enhance pitting and crevice attack. Should 304L show a susceptibility to these modes of attack, the solution would be to use a material less prone to pitting and crevice corrosion. The 316L and 317L grades of stainless steel would provide more resistance to pitting and crevice attack without introducing any known concerns in other areas.

Transgranular stress corrosion cracking can occur under the conditions already discussed for pitting and crevice corrosion, when the canister retains residual stress accumulated from the fabrication, welding, glass pouring, and cooling processes. In addition, the products of gamma radiolysis may accelerate this corrosion mechanism as well as pitting and crevice attack. Nickel additions to austenitic stainless steels impart greater resistance to transgranular stress corrosion cracking. Alloy 825 (Incoloy 825) is an example of a high-nickel stainless alloy that resists cracking in concentrated chloride-containing solutions.⁵ This alloy also contains molybdenum and titanium and is therefore more resistant to pitting, crevice, and intergranular corrosion than is 304L in higher strength ionic solutions. However, alloy 825 is considerably more expensive than 304L. It would therefore merit use as a canister material only if our investigations showed that a combination of high residual stress and more aggressive chemical conditions did develop in the repository environment than we initially expected, and that the performance of 304L in this circumstance was inadequate. If unstressed 304L shows adequate stress corrosion resistance, but stressed 304L does not, then the obvious solution is to overpack the 304L canister with a 304L overpack fabricated and welded by processes that minimize residual stress accumulation.

The final concern in connection with 304L stainless steel is that of phase stability. While 304L usually possesses an austenitic structure, this structure is metastable with respect to phase separation into ferritic

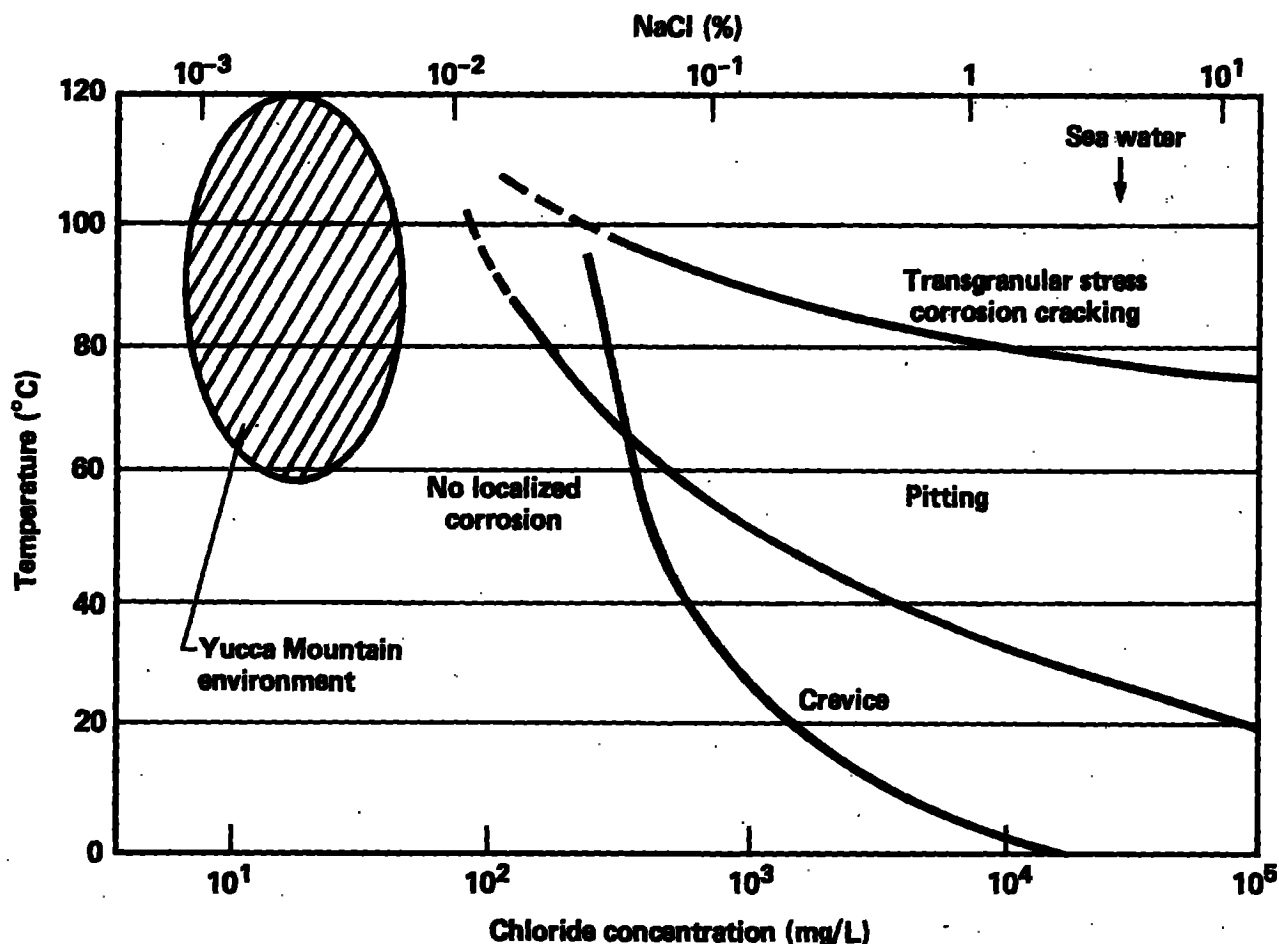


Figure B-2. Localized corrosion of type 304 stainless steel in water as a function of temperature and chloride concentration (modified from Nuttall and Urbanic, 1981¹⁶).

(body-centered cubic) and austenitic (face-centered cubic) phases of somewhat different compositions. This metastability is related to the overall alloy composition and is particularly sensitive to the carbon and nitrogen contents. By itself, a duplex ferrite-austenite structure is not necessarily detrimental to the corrosion behavior. During welding and resolidification, some ferrite normally occurs in the fusion zone. This, in fact, is a desirable reaction because a low level of ferrite prevents hot cracking in the welded region, but a high level of ferrite may result in embrittlement. The ferrite phase has less fracture toughness than the corresponding austenitic phase, and the ferritic structure has a tendency over a long period of time to transform to a very brittle sigma phase. The usual practice is to keep the ferrite content between 5 and 10% in the weld zone. With regard to the phase stability of 304L and other alternative austenitic stainless alloys previously discussed, an overall balance between the ferrite-stabilizing elements (Fe, Cr, Mo, Ti, Si, and Nb) versus the austenite-stabilizing elements (Ni, Mn, Cu, C, and N) must be maintained. When an increase or decrease of one of these elements is specified to raise the resistance to a particular form of corrosion, an adjustment in the others is often required to preserve the desirable austenitic structure. In addition to the high fracture toughness of austenite, as opposed to that of ferrite, the austenitic structure is more resistant to hydrogen-provoked embrittlement. Hydrogen can enter metal lattice during aqueous corrosion. Radiolytic decomposition of water also produces hydrogen. Hydrogen embrittlement effects are associated with a strained metal lattice and represent another form of stress corrosion cracking. The testing program addresses this possible deleterious effect by use of stressed and welded coupons in the test matrix. If hydrogen embrittlement or loss of fracture toughness develops as a problem, remedies include tighter specifications of the canister alloy composition or use of a relatively unstressed overpack of 304L.

The metals testing program is concerned with the reference material, AISI 304L stainless steel, and the three leading alternative materials, AISI 321L, AISI 316L, and Incoloy 825. These alternative materials were nominated because of their improved resistance to particular forms of localized and stress-assisted corrosion. The alternatives are 316L (more crevice and pitting corrosion resistant), 321 (more intergranular corrosion and intergranular stress corrosion resistant), and Incoloy 825 (more resistant to transgranular stress corrosion, also more resistant to pitting, crevice, and intergranular forms as well). Variations in the 304L composition, particularly toward premium grades with extra low carbon and low interstitial elements are included in the test program matrix, too. Some other stainless steels may be tested if time, resources, and the need exist. These primarily have compositions between 316L and Incoloy 825. They would be included in the test matrix if a concentrated electrolyte scenario were a realistic occurrence; and if the halide ion concentration developed near the canister surface were much higher than that of the reference J-13 water.

Survey tests will be run on (1) flat coupons to determine the general corrosion rate and susceptibility to pitting corrosion of the metals; (2) creviced coupons to determine the susceptibility to crevice attack; (3) stressed coupons, including welded specimens, to determine whether stress corrosion and hydrogen embrittlement are likely to occur; and (4) sensitized coupons to determine the likelihood of intergranular corrosion. Testing will also be done using tubular specimens that are heated from the center. The corrosion environments that will be investigated are (1) the hot "dry" steam plus air environment (100 to 300°C); (2) the wet-to-dry cycling conditions (80 to 100°C); (3) fully immersed (80 to 100°C) in water. Environments 2 and 3 will be investigated with and without the presence of gamma radiation in order to determine the effects of radiation and radiolysis reactions on corrosion. Some tests will be done using extreme environments to determine whether there is any possibility that specific nonuniform corrosion mechanisms will become important in the repository under unusual environmental conditions.

Following completion of the survey tests, a metal will be chosen for use in the preliminary waste package design. Should unexpected results occur during the survey tests, it may be necessary to extend the list of metals to solve particular problems. The metal selected for the preliminary design, and two alternative materials, will then be subjected to intensive long-term testing to confirm that performance in the repository (of metal components) can be confidently predicted.

While the borehole liners discussed as part of an alternative design for horizontal emplacement do not constitute a nuclear waste containment barrier, their use would require assessment of their expected service life in a tuff repository environment. The borehole liner should survive the 50-year retrieval period. The corrosion rate and corrosion attack pattern will therefore be determined on carbon steel under the environmental conditions just discussed for canisters and overpacks. Possible galvanic corrosion effects between the liner material and canister material will be addressed.

As a final remark, it is recognized that localized and stress-assisted forms of corrosion are the limiting factors in using 304L stainless steel (or any of the alternative alloys mentioned). The burden of proof in the metal barrier testing program is to show that the incidence of these types of occurrences falls to extremely low levels of probability under anticipated repository environmental conditions. The occurrence of localized and stress-assisted forms of corrosion has a statistical distribution for a given alloy/environmental combination. Advanced testing procedures incorporate statistical factors in conducting the tests and analyzing results. Examples of these kinds of tests include use of extreme value statistics to evaluate long-term localized corrosion observations and use of fracture mechanics stress corrosion testing procedures to relate stress, the distribution of fabrication-induced flaws in metals; and the resulting crack-propagation rates. Details of these testing procedures are discussed by Ailor.⁶ The objective of this work is to reduce the uncertainty of test results to low levels, consistent with the effort and expenditures in obtaining the results. Effort and money alone cannot buy experience, and while our experience with the proposed alloys is on the order of 50 years, the results of the metal testing will be tracked with the available information on these alloys to obtain the most reasonable extrapolation possible. Because stainless steels were developed for their corrosion resistance, the corrosion performance information on these materials is abundant and very well-documented.

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